

GB629412

Publication Title:

Manufacture of metallisable monoazo dyestuffs of the pyrazolone series

Abstract:

Abstract of GB629412

1-(41 Aminophenyl)-5-pyrazolones are manufactured by condensing an acylacetic ester with a p-nitrophenylhydrazine and then reducing the nitro group. An example describes the preparation of 1-(41-aminophenyl)-3-phenyl-5-pyrazolone from ethyl benzoylacetate. Ureas and thioureas of the foregoing pyrazolones are manufactured by condensing them with phosgene or thiophosgene, or with carbon disulphide, preferably in the presence of a small quantity of hydrogen peroxide, until free amino groups are no longer detectable. The urea and thiourea of 1-(411-amino-41-phenyl)-phenyl-3-methyl-5-pyrazolone are similarly prepared. Specification 486,660 is referred to. ALSO: Monoazo dyestuffs of the dipyrazolone series are manufactured by coupling one molecular proportion of 1 - diazo - 6 - nitro - 2 - hydroxy-naphthalene-4-sulphonic acid with a condensation product of phosgene or thiophosgene (or carbon disulphide) with two molecular proportions of a 5-pyrazolone derivative of the general formula $\text{FORM:0629412/IV (c)/1}$ (wherein Y represents a methyl, ethyl or phenyl group and Z a radical of the benzene series combined in the 1- and 4-positions or a radical of the diphenyl series combined in the 4- and 41-positions). Alternatively a monoazo dyestuff from 1 - diazo - 6 - nitro - 2 - hydroxy-naphthalene-4-sulphonic acid and a 5-pyrazolone derivative of the general formula above, together with a second molecular proportion of such a 5-pyrazolone derivative, are condensed with phosgene, thiophosgene or carbon disulphide until the primary amino groups disappear. The products have good affinity for cellulose, and may be treated in substance or on the fibre with metal-yielding agents, e.g. copper salts, giving orange-red or red dyeings. In examples: (1) 1 mol. of diazo - 6 - nitro - 2 - hydroxynaphthalene - 4-sulphonic acid is coupled in the presence of excess of sodium carbonate with 1 mol. of the urea of 1 - (41 - aminophenyl) - 3 - methyl - 5-pyrazolone, or with 1 mol. of the pyrazolone itself followed by treatment of the dyestuff and a further mol. of the pyrazolone with phosgene; (2) the urea in (1) is replaced by the corresponding thiourea, and (3) by the urea or thiourea of 1 - (411 - amino - 41 - phenyl) - phenyl - 3-methyl-5-pyrazolone. A table gives the properties of dyestuffs prepared from other coupling components of the type defined above. Specification 486,660 is referred to. Data supplied from the esp@cenet database - Worldwide

Courtesy of <http://v3.espacenet.com>

AMENDED SPECIFICATION

Reprinted as amended under Section 8 of the Patents Act, 1949.

PATENT SPECIFICATION

629,412



Application Date: Dec. 24, 1946. No. 37809/46.

Complete Specification Accepted: Sept. 20, 1949.

Index at acceptance:—Classes 2(iii), C2b(4: 31), C2b37(f3: i), C2d45; and 2(iv), P(1b4: 8: x).

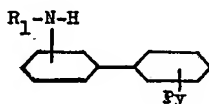
COMPLETE SPECIFICATION

Manufacture of Metallisable Monoazo Dyestuffs of the Pyrazolone Series

I, ROSLING MORGAN HUGHES, of 72 & 74, Cannon Street, London, E.C.4, Chartered Patent Agent, a British Subject, do hereby declare the nature of this invention (a Communication to me by J. R. Geigy, A—G., a body corporate organised according to the laws of Switzerland, of 215, Schwarzwaldallee, Basle, Switzerland) and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the manufacture of metallisable monoazo dyestuffs of the pyrazolone series.

Patent Specification No. 486,660, as open to public inspection under Section 91 (4) of the Patents and Designs Acts, 1907 to 1946, describes *inter alia* the manufacture of metallisable azo dyestuffs by coupling the diazo-compound of, for example, an ortho-aminonaphthol sulphonic acid with a pyrazolone derivative of the general formula:—

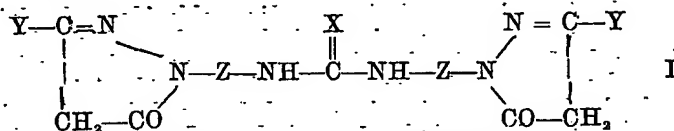


25

wherein R_1 is hydrogen or the residue of an organic acid, including a dicarboxylic acid, e.g., carbonic acid, oxalic acid, fumaric acid, maleic acid, phthalic acid, sulphophthalic acid, in which two or only one carboxylic acid residue may be substituted, and Py is a pyrazolone capable of being coupled; but no specific mention is made of monoazo dyestuffs of dipyrazolone-ureas.

It has been found that valuable metallisable monoazo dyestuffs of the pyrazolone

series, which, surprisingly, are distinguished by a good affinity for cellulose fibres, can be produced when molar quantities of the nitrated diazo compound of 1-amino-2-hydroxynaphthalene-4-sulphonic acid, i.e., 1-diazo-6-nitro-2-hydroxy naphthalene-4-sulphonic acid, are combined, in a slightly acid, a neutral or a slightly alkaline medium, with molar quantities of a dipyrazolone of the general formula I:—



50

wherein X denotes an O or S atom;

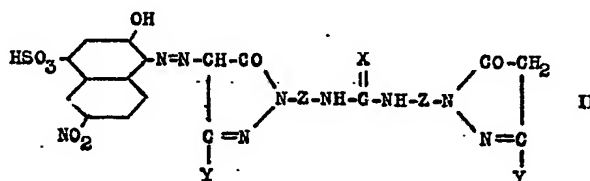
Y denotes a methyl, ethyl or phenyl group, and

Z denotes a member of the group of radicals of the benzene series combined

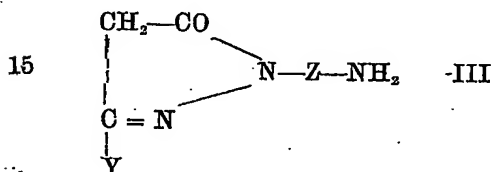
[Price 2/-]

in the 1- and 4-positions or a member of the group of radicals of the diphenyl series combined in the 4- and 4'-positions.

According to the invention a metallisable dyestuff of the dipyrazolone series of the general formula II



is produced when a molar quantity of 1-diazo-6-nitro-2-hydroxynaphthalene-4-sulphonic acid is caused to react with a condensation product of phosgene or thiophosgene and two molecular parts of a 5-pyrazolone derivative of the general formula III:—



In these general formulæ II and III, X, Y, and Z have the same meaning as given above with respect to the general formula I of the dipyrazolone.

The new dyestuffs are reddish-brown to dark powders. They can be converted into complex metal compounds by treatment with metal-yielding agents in substance or on the fibre by the usual methods. The complex copper compounds are especially valuable owing to their excellent fastness to light. The coppering may be effected in known manner, for example, with copper sulphate in a neutral bath or in a bath which has been slightly acidified with acetic acid, or in the presence of alkali tartrates in a slightly alkaline bath. In this way, orange-red or red dyeings are obtained which are fast to light and alkali and are frequently astonishingly fast to moisture.

Especially valuable on account of the ease with which they are obtained and their better capacity for going on cellulose fibres are the monoazo dyestuffs obtained from the series of the 1-(4'-aminophenyl)-3-methyl-5-pyrazolone ureas. The monoazo dyestuffs obtained from 1-(4'-amino-4'-phenyl)-phenyl-3-methyl-5-pyrazolone ureas are distinguished, on the other hand, by the especially good fastness to water of the dyeings, treated with copper salts, on cellulose fibres.

In comparison with the disazo dyestuffs obtained from the same dipyrazolone derivatives, the affinity for cellulose fibres is surprisingly good, because, in other cases, generally the loss of one azo group from the conjugated system causes a disazo dyestuff to become a monoazo dyestuff having a considerably lower affinity for cellulose fibres.

The same valuable metallisable monoazo dyestuffs are obtained when monoazo dyestuffs, obtained from 1-diazo-6-nitro-2-hydroxynaphthalene-4-sulphonic acid and a 1-(4'-aminophenyl)-5-pyrazolone derivative or a 1-(4'-amino-4'-phenyl)-phenyl-5-pyrazolone derivative of the general formula III above, together with a further molecule of such a 1-(4'-aminophenyl)-5-pyrazolone derivative or of such a 1-(4'-amino-4'-phenyl)-phenyl-5-pyrazolone derivative, are condensed with phosgene, thiophosgene or carbon disulphide until the primary amino groups disappear.

The invention is illustrated but not limited by the following examples. The parts are by weight unless otherwise stated, and the temperatures are Centigrade.

EXAMPLE 1.

29.5 parts of 1-diazo-6-nitro-2-hydroxynaphthalene-4-sulphonic acid are combined with 40.4 parts of the urea of 1-(4'-aminophenyl)-3-methyl-5-pyrazolone in the presence of an excess of sodium carbonate to form the monoazo dyestuff. After repeated stirring while cooling with ice, the diazo compound disappears. The dyestuff is isolated with sodium chloride. The dried dyestuff is a dark powder which dissolves in water giving a red colour and in concentrated sulphuric acid giving an orange colour and dyes cellulose fibres in brown-orange shades. By after-coppering, the colour is displaced towards red and the fastness of the dyeing to moisture and light is considerably improved.

The same dyestuff is obtained when 29.5

parts of 1-diazo-6-nitro-2-hydroxynaphthalene-4-sulphonic acid are coupled with 18.9 parts of 1-(4'-aminophenyl)-3-methyl-5-pyrazolone in a sodium carbonate alkaline solution, and the aminomonoazo dyestuff obtained together with 18.9 parts of 1-(4'-aminophenyl)-3-methyl-5-pyrazolone are condensed in sodium carbonate alkaline solution with phosgene until free amino groups are no longer detectable. The dyestuff has the same properties as that described above.

The urea of 1-(4'-aminophenyl)-3-methyl-5-pyrazolone can be produced by known methods by condensing 37.8 parts of 1-(4'-aminophenyl)-3-methyl-5-pyrazolone in sodium carbonate-alkaline solution with phosgene until free amino groups are no longer detectable. The urea is a colourless powder.

EXAMPLE 2.

29.5 parts of 1-diazo-6-nitro-2-hydroxynaphthalene-4-sulphonic acid are combined with 42 parts of the thiourea of 1-(4'-aminophenyl)-3-methyl-5-pyrazolone in the presence of an excess of sodium carbonate to form the monoazo dyestuff. After stirring for several hours while cooling with ice, the diazo compound disappears. The dyestuff is isolated with sodium chloride. The dried dyestuff is a dark powder which dissolves in water giving an orange-red colour and in concentrated sulphuric acid giving an orange colour and dyes cellulose fibres in brown-orange shades. By after-treatment with copper sulphate, the colour is displaced towards red and the fastness to moisture and light is considerably improved.

The thiourea of 1-(4'-aminophenyl)-3-methyl-5-pyrazolone is obtained when 37.8 parts of 1-(4'-aminophenyl)-3-methyl-5-pyrazolone is treated, in sodium carbonate-alkaline solution, with thiophosgene until free amino groups are no longer detectable, or when 1-(4'-aminophenyl)-3-methyl-5-pyrazolone is condensed with carbon disulphide in the presence of a small quantity of hydrogen peroxide until free amino groups are no longer detectable.

The production of 1-(4'-aminophenyl)-5-pyrazolones will be explained with the aid of the following example:—If 19.2 parts of ethyl benzoylacetate are condensed in boiling alcohol with 15.3 parts of *p*-nitrophenylhydrazine, the 1-(4'-nitrophenyl)-3-phenyl-5-pyrazolone is obtained in good yield. The compound is in the form of yellow needles having a melting point of 201–202°. By reduction with iron, the corresponding 1-(4'-amino-

phenyl)-3-phenyl-5-pyrazolone is obtained which is isolated in the form of the colourless crystalline hydrochloride.

If other acylacetic esters or substituted *p*-nitrophenylhydrazines are caused to react with each other in equivalent quantities, the corresponding 1-(4'-nitrophenyl)-5-pyrazolones and 1-(4'-aminophenyl)-5-pyrazolones are obtained which have very similar properties to those of the 1-(4'-aminophenyl)-3-phenyl-5-pyrazolone hereinbefore described.

EXAMPLE 3.

29.5 parts of 1-diazo-6-nitro-2-hydroxynaphthalene-4-sulphonic acid are combined, in the presence of an excess of sodium carbonate, with 55.6 parts of the urea of 1-(4'-amino-4'-phenyl)-phenyl-3-methyl-5-pyrazolone in aqueous solution and with cooling by means of ice. After stirring for several hours at 0–10°, the diazo compound vanishes. The dyestuff is isolated with sodium chloride. The dried dyestuff is a dark powder which dissolves in water giving a red colour and in concentrated sulphuric acid giving an orange colour and dyes cellulose fibres in brown-orange shades. By treating the dyeings with copper salts by the usual methods, an orange red is obtained and the fastness to moisture and light is considerably improved.

The urea of 1-(4'-amino-4'-phenyl)-phenyl-3-methyl-5-pyrazolone is obtained by passing phosgene into a solution of 53 parts of the aminopyrazolone mentioned in 500 parts of water in the presence of an excess of sodium carbonate at room temperature until free amino groups are no longer detectable.

The corresponding thiourea is obtained under the same conditions by passing in thiophosgene until the primary amino groups disappear. The sodium carbonate-alkaline solution of 1-(4'-amino-4'-phenyl)-phenyl-3-methyl-pyrazolone may also be condensed with carbon disulphide and hydrogen peroxide in known manner to form the thiourea.

The monoazo dyestuff produced from 29.5 parts of 1-diazo-6-nitro-2-hydroxynaphthalene-4-sulphonic acid and from 57.2 parts of the thiourea of 1-(4'-amino-4'-phenyl)-phenyl-3-methyl-5-pyrazolone under the conditions described above is very similar in its properties to the dyestuff described above. Similar dyestuffs of the same kind can be produced in accordance with the invention from components shown in the following table:—

TABLE.

5	No.	Diazo compound	Dipyrazolone according to Formula I.	Colour shade of the coppered dyeing on cellulose fibres
	1.	1 - diazo - 6 - nitro - 2- hydroxynaphthalene - 4- sulphonic acid	Urea of 1 - (4 ¹ - amino- phenyl) - 3 - phenyl- 5 - pyrazolone - - -	red
10	2.	"	Urea of 1 - (4 ¹ - amino- phenyl) - 3 - ethyl- 5 - pyrazolone - - -	
	3.	"	Urea of 1 - (4 ¹ - amino- 2 ¹ - chlorophenyl) - 3- methyl - 5 - pyra- zalone - - -	
15	4.	"	Urea of 1 - (4 ¹ - amino- 2 ¹ - methyl - phenyl)- 3 - methyl - 5 - para- zalone - - -	"
20	5.	"	Thiourea of 1 - (4 ¹ - amino - 2 ¹ - methyl- phenyl) - 3 - methyl- 5 - pyrazolone - - -	"
25	6.	"	Urea of 1 - (4 ¹ - amino- 3 ¹ - chlorophenyl) - 3- methyl - 5 - pyra- zalone - - -	"
30	7.	"	Urea of 1 - (4 ¹ - amino- 2 ¹ - methoxyphenyl)- 3 - methyl - 5 - pyra- zalone - - -	"
35	8.	"	Urea of 1 - (4 ¹ - amino- 2 ¹ - bromophenyl) - 3- methyl - 5 - pyra- zalone - - -	"
	9.	"	Urea of 1 - (3 ¹ :2 ¹¹ - di- methyl - 4 ¹¹ - amino-4 ¹ - phenyl) - phenyl - 3- methyl - 5 - pyrazolone	"
40	10.	"	Thiourea of 1-(4 ¹ -amino- 3 ² - methylphenyl) - 3- methyl - 5 - pyrazoline	"
45	11.	"	Thiourea of 1-(4 ¹ -amino- 2 ¹ - chlorophenyl) - 3- methyl - 5 - pyrazolone	"
	12.	"	Thiourea of 1-(4 ¹ -amino- phenyl) - 3 - phenyl-5- pyrazolone - - -	"
50	13.	"	Thiourea of 1-(4 ¹¹ -amino- 4 ² -phenyl) - phenyl-3- methyl - 5 - pyrazolone	"

No claim is made herein to a process as hereinafter claimed, in so far as it may form a step in a process for the production of disazo dyestuffs claimed in the specification of Patent No. 632,944 (Application No. 911/47) J. R. Geigy A.-G., with the Convention priority date 27th December, 1945, but not being a prior publication.

Having now particularly described and

ascertained the nature of my said invention and in what manner the same is to be performed, as communicated to me by my foreign correspondents, I declare that, subject to the foregoing disclaimer, what I claim is:—

1. The manufacture of a metallisable monoazo dyestuff of the dipyrazolone series wherein a molar quantity of 1-diazo-6-nitro - 2-hydroxynaphthalene-4-sulphonic

acid is caused to react with a molar quantity of a dipyrazolone of urea or thiourea as hereinbefore defined by formula I so as to couple with the carbon atom in the 4 position of one of the pyrazolone rings and produce the monoazo dyestuff.

2. The manufacture of a metallisable monoazo dyestuff of the dipyrazolone series of the general formula II as hereinbefore defined wherein a molar quantity of 1-diazo-6-nitro-2-hydroxynaphthalene-4-sulphonic acid is caused to react with a condensation product of phosgene or thiophosgene and two molecular parts of a 5-pyrazolone derivative of the general formula III as hereinbefore defined.

3. A modification of the process according to claim 2, wherein a molar quantity of a monoazo dyestuff obtained from 1-diazo-6-nitro-2-hydroxynaphthalene-4-sulphonic acid and a 5-pyrazolone derivative of the general formula III, together with a further molar quantity of such a 5-pyrazolone derivative, are condensed with phosgene, thiophosgene or carbon disulphide, and the reaction is continued until the primary amino groups disappear.

4. The manufacture of a monoazo dyestuff according to the process specified in any of the Examples 1 to 3.

5. The manufacture of monoazo dyestuffs according to claim 1 or 2, from components as specified in the foregoing Table.

6. Monoazo dyestuffs capable of being metallised, whenever prepared or produced by the process according to any of the Examples 1 to 3.

7. Monoazo dyestuffs whenever prepared by the process according to claim 1 or 2, from components as specified in the foregoing Table.

8. Metallisable monoazo dyestuffs of the dipyrazolone series, whenever prepared or produced by the processes of manufacture particularly described and ascertained or by their obvious chemical equivalents.

9. The manufacture of monoazo dyestuffs according to claim 1 or 2, wherein the product is after-treated in substance or on the fibre with a metal-yielding agent, especially a copper yielding agent.

10. A process of dyeing wherein the material is dyed by means of a monoazo dyestuff as claimed in any preceding claim, and wherein, if desired, the dyestuff is subjected to after-treatment in substance or on the fibre with a metal-yielding agent.

11. Cellulose material whenever dyed with a monoazo dyestuff by a process according to claim 10.

Dated the 24th day of December, 1946.

For the Applicant,
HENRY IMRIE & CO.,
Chartered Patent Agents,

72 & 74, Cannon Street, London, E.C.4.